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Extended Abstracts

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Jarosław Kania
Ewa Kmiecik

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Mineral and thermal water

4.3
Hydrogeochemical characteristics of mineral and thermal waters

title: **Stable isotopes of dissolved inorganic carbon and sulphur-bearing species in mineral and thermal waters from central Portugal**

author(s): **Manuel J. F. Morais**
Centre for Geophysics of the University of Coimbra, Portugal,
manuelmorais@engenheiros.pt

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1. INTRODUCTION

There are many springs of mineral and thermal waters associated with the Hercynian Beiras Batholith granites of Central Portugal, which intruded meta-sedimentary rocks of Palaeozoic age. These low enthalpy thermomineral systems reflect the deep circulation of meteoric waters in fractured granites. All waters studied have similar chemical characteristics: pH varies between 8 and 9.3; Na^+ is the dominant cation (representing over 90% of the total cations); HCO_3^- is the most representative anion, followed by Cl^- and/or F^- (always > 10 mg/L); and all of them are strongly reduced (as revealed by reduced sulphur (HS^-) and reduced nitrogen (NH_4^+)) and have very low Mg^{2+} contents (usually < 0.15 mg/L). Temperature ranges between 18 and 66°C, and total dissolved solids between ~200 and ~500 mg/L. Both natural springs and boreholes as deep as 500 meters were studied.

2. EXPERIMENTAL PROCEDURES

Samples for $^{13}C/^{12}C$ measurements were obtained by precipitation of the total dissolved inorganic carbon (DIC) as $SrCO_3$ by means of $SrCl_2$. The precipitate was filtered and dried without any contact with atmospheric air. Gas extraction was done by acidification with 103% H_3PO_4 and purification by criogenic distillation. Dissolved sulphide was collected as ZnS precipitated by addition of zinc acetate to the water, and later converted to Ag_2S by means of $AgNO_3$. Following filtration of the ZnS, the remaining water was acidified and treated with $BaCl_2$ to precipitate dissolved sulphate as $BaSO_4$. All isotopic analyses were done at the Stable Isotope Laboratory, University of Salamanca. The isotopic values are reported in the usual delta notation (δ‰) relative to V-PDB ($\delta^{13}C$) and CDT ($\delta^{34}S$).

3. RESULTS AND DISCUSSION

3.1. $\delta^{13}C$ of the dissolved inorganic carbon

The $\delta^{13}C_{VPDB}$ values of the total dissolved inorganic carbon (TDIC) in groundwaters range from –16.9 to –10.5‰. This range of $\delta^{13}C_{DIC}$ values is acompanied by a large variation of TDIC contents. The observed linear relation between TDIC and $\delta^{13}C$ (Fig. 1) suggest that inorganic carbon in the studied waters derives from more than one source: measured $\delta^{13}C$ values can not be attributed to isotope fraccionation between soil-CO_2 and DIC only.

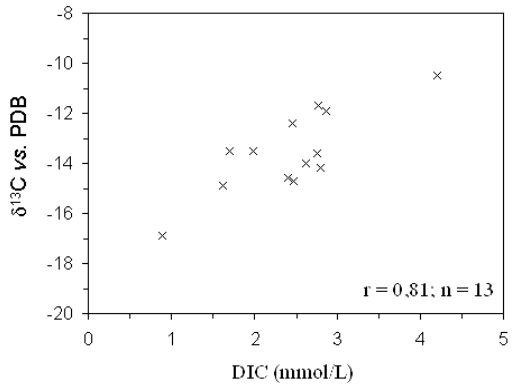

Figure 1. Relation between Total Dissolved Inorganic Carbon and $\delta^{13}C$.

A gaseous source, isotopically havier than the organic C of soil-CO_2 (such as regional deep mantle-derived or metamorphic flux of CO_2), must be invoked.

3.2. $\delta^{34}S$ of sulphur-bearing species (SO_4^{2-}; HS^-)

The $\delta^{34}S$ of sulphur-bearing species shows a remarkable variability: $\delta^{34}S_{CDT}$ (SO_4^{2-}) ranges from +6 to +44 ‰; $\delta^{34}S_{CDT}$ (HS^-) ranges from –25 to +2‰. Sulphate is always enriched in ^{34}S relative to reduced sulphur (HS^-). This isotopic difference ($\Delta^{34}S=\delta^{34}S$ (SO_4^{2-})–$\delta^{34}S$ (HS^-); mean value = 28.5‰) is interpreted as the result of biogenic reduction of sulphate occuring in these waters. An apparent reduction trend is seen on Figure 2.

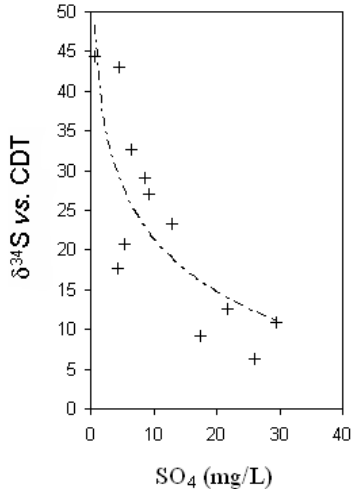

Figure 2. Comparison of sulphate concentrations and $\delta^{34}S$ values.

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